

PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improvements in and relating to Halogen-Containing Polymer Compositions

We, B.X. PLASTICS LIMITED, a British Company, of Larkshall Road, Highams Park, London, E.4, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to materials for improving the heat and light stability of chlorine-containing homopolymers or copolymers.

When chlorine-containing homopolymers or copolymers are subjected to thermal treatment, for example, during their fabrication by milling, calendering or extrusion, degradation occurs in the polymeric material, resulting in undesirable changes in the colour or clarity of the material. If degradation continues other physical properties are eventually affected, notably certain mechanical and electrical properties. These undesirable changes can also be brought about by the action of light. It has been found possible to delay the onset of the degradation by the use of thermal stabilisers, and the compounds that have been used as stabilisers are numerous and varied. However, there is a limit to the degree of protection afforded to unplasticised polymeric material by even the best of known stabilisers, and a yellow discolouration always develops when such material is heated at, for example, 180°C for 10 minutes, and this effect cannot be prevented by merely increasing the amount of the known stabiliser used. The present invention is concerned with this problem of degradation due to the effect of heat and/or light, and the invention is based on the observation that by incorporating in the stabiliser-polymer mixture two extra components which act in a synergistic manner with the normal stabiliser, stages in the degradation process which are

not affected by the normal stabiliser are prevented or delayed.

This invention provides a chlorine-containing polymer composition comprising a mixture of a chlorine-containing homopolymer or copolymer sensitive to heat and/or light degradation, together with a system consisting of at least one member drawn from each of categories (a), (b) and (c), wherein

(a) represents a stabiliser for chlorine-containing polymers which comprises an organic-metallic compound in which the metal atom is lithium, sodium, potassium, magnesium, calcium, zinc, strontium, cadmium, barium, aluminium, tin or lead, or a mixture of any two or three of such organic-metallic compounds, provided that the stabiliser does not solely comprise barium laurate or cadmium laurate or dibasic lead phthalate, nor contain a mixture comprising organic-barium, organic-cadmium or organic-tin compounds.

(b) represents a sulphur-containing organic or organo-metallic compound having a boiling point at atmospheric pressure not below 200°C, and that does not contain chains of more than two consecutive sulphur atoms and in which at least one of the sulphur atoms has at least one lone electron pair, excepting mercapto-benzimidazole, mercapto-benzothiazole and their salts.

(c) represents an organic antioxidant capable of inhibiting chain reactions leading to degradation in the chlorine-containing homopolymer or copolymer; provided also that the members drawn from each category are chemically distinct, such that at least three separate chemical compounds are present in admixture with the chlorine-containing polymer or polymers.

Chlorine-containing homopolymers or co-

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polymers that may be used in compositions according to the present invention include homopolymers are copolymers in which the monomer, or at least one of the monomers in a copolymers, respectively, is a chlorine-containing olefinically unsaturated compound, said homopolymer or copolymer being sensitive to heat and/or light degradation.

Mixtures of homopolymers and/or copolymers may also be used in the compositions according to the invention.

Examples of monomers from which the chlorine-containing homopolymers and copolymers may be derived include vinyl chloride, vinylidene chloride and cis- or trans-1:2-dichloroethylene; the copolymers may be derived from the above mentioned monomers and, for example, vinyl acetate. Post-chlorinated polymers, for example, post-chlorinated polyvinyl chloride, and graft or block copolymers derived from the above-mentioned monomers may also be used in the compositions of the present invention. The post-chlorinated polymer may be, for example, polyvinyl chloride or a vinyl chloride copolymer which has been further chlorinated in suspension under the influence of ultra-violet irradiation, to give a product having a chlorine content in the range of 55 to 70% by weight and containing only a minor proportion of 1:1-dichloroethylene units based on the total weight of dichloroethylene units present.

The homopolymers and copolymers found to be especially suitable are polyvinyl chloride, a vinyl chloride/vinylidene chloride copolymer containing 3—4% of vinylidene chloride, and a vinyl chloride/vinyl acetate copolymer containing about 10% of vinyl acetate.

The improvements to the heat and/or light stability of the homopolymers and copolymers may be obtained regardless of the method by which the polymers have been prepared. For example, the polyvinyl chloride homopolymer may be prepared by an emulsion, suspension or bulk polymerisation method, whilst the vinyl chloride/vinyl acetate copolymer may be prepared by an emulsion, suspension, or solution method, the invention being applicable to the homopolymer or copolymer obtained by any of these methods.

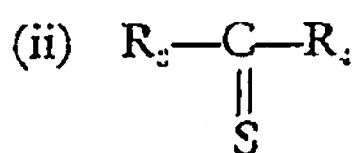
The stabiliser (a) for the chlorine-containing polymers is preferably an organo-tin or organo-thio-tin compound, or a mixture of an organo-tin and an organo-thio-tin compound, or a suitable organic-barium or organic-cadmium compound, or a mixture of an organic-barium and an organic-cadmium compound.

Examples of stabilisers with which components (b) and (c) in the compositions of the present invention act in a synergistic manner include dibutyl tin maleate prepolymer, cadmium and barium stearate, dibutyl tin β -mercapto-propionate/2-ethyl-hexyl

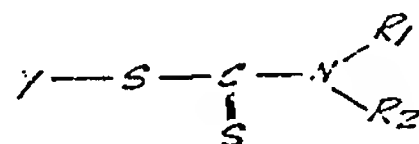
maleate, and dibutyl tin bis (2-ethyl-hexylthio-glycollate).

Organic-lead compounds may be used, but they impart a colour to the composition which would mask the effect of the invention on the yellowing of the polymer. The composition would still improve other physical properties affected by the degradation.

The sulphur-containing organic or organo-metallic compound which is used as component (b) in a composition according to the present invention may be any one of the compounds covered by the following general formulae:—



(iii)

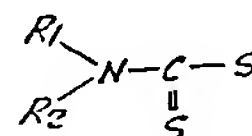


wherein:—

R_1 and R_2 are the same or different, and may be an alkyl, alkenyl, alkynyl, aralkyl, aryl, alkyl-aryl or cycloalkyl radical, or a radical containing a heterocyclic ring containing nitrogen, oxygen or sulphur, or R_1 or R_2 , but not both, may be a hydrogen atom.

R_3 and R_4 are the same or different, and may be a radical defined for R_1 and R_2 , or may be a primary or secondary alkyl-, aralkyl-, aryl-, alkyl-aryl- or cycloalkyl-amino radical, or R_3 or R_4 , but not both, may be a hydrogen atom.

Y may be the group



or may be a metal atom, for example, tin or zinc. If the metal atom has a valency greater than one, then the remaining groups attached to the metal atom may each be any one of the groups R_1 , R_2 , R_3 , R_4 and Y, but where Y is not a metal atom.

R_1 , R_2 , R_3 and R_4 may be substituted by one or more of the following groups:—
—OH, —COOH, $>C=O$, —CHO, —NH₂, sulphonic acid, mercapto, halogen. A replaceable hydrogen atom in such a group may be substituted by R_1 or R_2 or a metal atom. If the metal atom has a valency greater than one, then the remaining groups attached to the metal atom may each be any one of the groups R_1 , R_2 , R_3 , R_4 and Y, but where Y is not a metal atom. These groups may or may not contain a sulphur atom.

It must also be understood that R_1 and R_2 may be joined either through a metal atom acting as a substituent as defined above, or by carbon, nitrogen, sulphur, or oxygen. R_3 and R_4 may be joined in a similar manner.

The metal atoms mentioned above are selected from those suitable for use in stabiliser (a) for the polymer as hereinbefore defined.

The sulphur-containing compounds as defined above must have a boiling point at atmospheric pressure not below 200°C , must contain at least one sulphur atom with at least one lone electron pair, and should not preferably be oxidisable to a compound having an objectionable colour, if discolouration is to be particularly avoided.

Sulphur itself, and inorganic sulphur compounds, do not act in the synergistic manner characteristic of the present invention. Unsaturated heterocyclic compounds in which sulphur is present solely as a member of the heterocyclic ring are not as suitable as the above classes of compounds.

Examples of the classes of sulphur-containing compounds that may be used are: alkyl or aryl sulphides, mercapto carboxylic acids or esters thereof, monothio or dithio dicarboxylic acids or esters or anhydrides thereof, thio glycols or esters or ethers thereof, hydroxy alkyl (or aryl) sulphides or esters or ethers thereof, polyesters of these glycols and acids described above, aromatic thiols, thio-ureas, dithio-carbonates or dithio-carbamates.

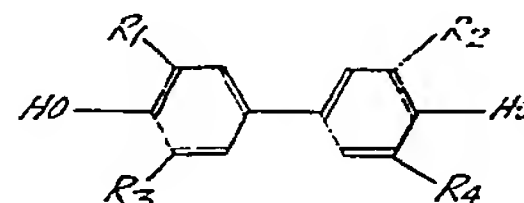
Particular examples of such compounds include: thioglycollic acid, lauryl thioglycollate, nonyl thioglycollate, thiodiglycollic acid, dithiodiglycollic acid, β mercaptopropionic acid, $\beta\beta^1$ thiodipropionic acid, $\beta\beta^1$ dithiodipropionic acid, dilauryl $\beta\beta^1$ thiodipropionate, $\beta\beta^1$ dihydroxy-ethyl sulphide, bis (n-dodecyloxy-ethyl) sulphide, 4-4¹ thio bis-(6-tertiary butyl meta-cresol), dibutyl tin bis (dibutyl dithiocarbamate), zinc bis (dibutyl dithiocarbamate), zinc diethyl dithiocarbamate, dibutyl tin dithiodiglycollate, naphthalene thiol, dibutyl tin bis (diphenyl dithiocarbamate) and dibutyl tin bis (diphenyl thiourea dithiocarbamate). The last mentioned is prepared from a dichloro stannic compound, carbon disulphide and diphenyl thiourea.

The organic antioxidant may be an antioxidant suitable for use with polyolefines, and is preferably a nuclear substituted phenol, an aromatic primary or secondary amine, an N-substituted *p*-amino phenol, or a compound containing a nitrogen heterocyclic ring in which the nitrogen atom bears a replaceable hydrogen atom.

Examples of suitable antioxidants are 2:6 di-tertiary butyl 4-methyl phenol, 2:4 dimethyl 6-tertiary butyl phenol, 2:2¹ methylene bis [4-methyl (or 4-ethyl) 6-tertiary butyl phenol], resorcinol monobenzoate, *p*-octyl phenyl salicylate, bisphenols (for example, bisphenol A), various di-hydroxy-biphenyls,

pentaerythritol, α -phenol indole, diphenylamine, N-stearoyl *p*-amino phenol and N-lauroyl *p*-amino phenol. The antioxidant may contain sulphur, an example being 4,4¹ thio bis 6-tertiary butyl meta-cresol.

Examples of the various di-hydroxy-biphenyls are indicated by the formula:



wherein R_1 , R_2 , R_3 and R_4 may each be tertiary butyl, ethyl, or methyl.

The sulphur-containing compound and the antioxidant may each be used in an amount of from 0.001 to 3% by weight based on the weight of the polymer. The ratio of the amounts of these two components may vary between wide limits, but the sulphur-containing compound added as component (b) preferably comprises 20—80% by weight of the mixture of components (b) and (c). Advantageously, equal amounts by weight of (b) and (c) are added to the polymer composition.

The chlorine-containing homopolymers or copolymers that may be used in the composition may be either plasticised or unplasticised. Although it is known to add certain antioxidants to plasticised polymers in order to prevent or inhibit the oxidation of the plasticiser, these known antioxidants are in themselves incapable of stabilising rigid (that is, unplasticised) chlorine-containing polymers. The present invention improves the heat and/or light stability of both unplasticised and plasticised chlorine-containing polymers.

The compositions according to the present invention may also contain a processing aid, which is a polymeric compound which enables a polymer composition to be processed at a lower temperature than normal, and facilitates blending and gelling, thereby improving the appearance and surface finish of mouldings and extrusions. The processing aid may comprise acrylic compounds, for example it may be an elastomeric butadiene-styrene or alkyl acrylate copolymer to which methyl methacrylate or methyl methacrylate-styrene copolymer side chains are grafted, for example as described in British Patent 975,421. However, it may also impart some yellow colour to the finished material. The stabiliser/antioxidant composition according to the present invention substantially reduces this yellowing effect due to the processing aid.

The composition may also contain a metal sequestering agent as, for example, triphenyl phosphite, epoxidised soya bean oil and similar compounds normally associated with organometallic compounds used as stabilisers for chlorine-containing polymers.

5 The composition may also contain any of the
usual colouring and toning pigments to allow
a variety of attractive transparent materials to
be made. Fillers, for example, titanium dioxide
or silica, may also be used, but, in opacifying
the material in this way, the effect of the
stabiliser/antioxidant composition of the pre-
sent invention in improving the colour and
clarity of the polymer will be masked by the
10 filler.
In a process for the manufacture of poly-
meric material having an improved heat and/or
light stability, components (a), (b) and (c),
together with any other additives, may be
15 mixed with or added to the chlorine-containing

polymer at any stage before fabrication. The
components and/or other additives may be
added separately or in a single operation,
methods known to those skilled in the art
being used to ensure that an even distribution
of the components and/or additives throughout
the mixture is achieved.
The following Examples illustrate the in-
vention, the parts and percentages being by
weight (the words "Geon" and "Breon" are
25 Registered Trade Marks):—

EXAMPLE 1

The following compositions were prepared,
A and B being for comparison purposes only.

	A	B	C
Breon 202 (formerly Geon 202): a copolymer formed from 96% of vinyl chloride and 4% of vinylidene chloride	100	100	100
Component (a): dibutyl tin maleate prepolymer	2	4	2
Component (b): naphthalene thiol	—	—	0.1
Component (c): 2:6 di-tertiary butyl 4-methyl phenol	—	—	0.1
Wax OP: a modified montan wax, melting point 102—106°C., acid number 10—15, and specific gravity 1.03	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$

30 These compositions were milled at 165—
170°C and specimens were pressed at 190°C
for varying lengths of time. The optical
density of each specimen was measured at
35 4000Å and the results are recorded below. The

optical density provides a measure of the free-
dom from colour and haze in the sample. The
higher the optical density, the poorer the
colour.

Time in minutes of pressing at 190°C.		5	10	15	20	30	45	60
Optical density	A	5.34	6.15	6.45	8.05	8.56	11.0	14.6
per thou x 10 ³	B	5.32	6.42	6.52	7.42	8.38	11.4	18.2
	C	4.45	5.22	6.15	6.54	7.32	10.6	13.5

5 These results show that the composition C (according to the present invention) had a better retention of clarity due to a decrease in the amount of yellowing resulting from degradation. The results also show that such an improvement cannot be achieved by merely increasing the concentration of dibutyl tin maleate prepolymer (a known stabiliser) in the composition A.

EXAMPLES 2—8

10 Compositions containing as components (b) and (c) the compounds shown below and made up according to the following general compositions, were milled at 165—175°C and pressed for 30 minutes at 190°C. The optical density of each specimen was measured at 4000Å. The optical density increases with an increase in yellowing due to degradation in the specimens.

General composition	Parts
Breon 202 (formerly Geon 202)	100
Dibutyl tin maleate prepolymer	2
Antioxidant	0.1
Sulphur compound	0.1
Wax OP	0.25

Example	Optical density per thou $\times 10^3$	Antioxidant component (c)	Sulphur compound component (b)
2	7.50	2:6 ditertiary butyl 4-methyl phenol	dilauryl $\beta\beta^1$ thiodipropionate
20 3	7.22	2:6 ditertiary butyl 4-methyl phenol	$\beta\beta^1$ dihydroxy-ethyl sulphide
4	8.24	2:6 ditertiary butyl 4-methyl phenol	dibutyl tin dithiodiglycollate
5	7.72	2:6 ditertiary butyl 4-methyl phenol	dibutyl tin bis (diphenyl dithio carbamate)
6	8.30	2:6 ditertiary butyl 4-methyl phenol	dibutyl tin bis (diphenyl thiourea dithiocarbamate)
7	8.30	pentaerythritol	dilauryl $\beta\beta^1$ thiodipropionate
8	6.41	diphenylamine	dilauryl $\beta\beta^1$ thiodipropionate

25 As can be seen by comparing the above values of optical density with the corresponding values given in Example 1 for compositions A and B (not containing components (b) and (c)), that is, 8.56 and 8.38 respectively, all the above Examples show an improvement in their retention of colour and clarity.

EXAMPLES 9—10

The following compositions containing a homopolymer of vinyl chloride prepared by a bulk polymerisation method and having a 'K' value of 65 were prepared:

	Example 9	Example 10
Homopolymer	100 parts	100 parts
Component (a)	2 parts of dibutyl tin maleate prepolymer	2 parts of dibutyl tin maleate prepolymer
Component (b)	0.2 parts dilauryl $\beta\beta^1$ thio dipropionate	0.1 part $\beta\beta^1$ dihydroxy ethyl sulphide
Component (c)	0.2 parts resorcinol monobenzoate	0.1 part p-octyl phenyl salicylate

For comparison purposes the following composition was also prepared:

- 5 100 parts of the homopolymer
 2 parts of dibutyl tin maleate prepolymer
 0.25 parts Wax OP.

Each of the three compositions was milled at 165—170°C for 10 minutes, and specimens were pressed at 180°C for 30 minutes. The optical density of each specimen was measured at 4000A and the results are shown below.

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Composition	Optical density per thou. x 10 ³
Example 9	4.95
Example 10	3.88
Comparison	11.5

- 15 These results show that compositions prepared in accordance with the present invention had a better retention of clarity than a composition which did not contain each one of the components (a), (b) and (c).

EXAMPLE 11

- 20 A composition containing 5 kg of a vinyl chloride/vinyl acetate copolymer (containing 10% of vinyl acetate units), 100 grams of dibutyl tin bis (2 ethyl hexyl thioglycollate) as component (a), 12.5 grams of dilauryl thio-dipropionate as component (b), 12.5 grams of 2,6 ditertiary butyl 4-methyl phenol as component (c) and 15 grams of Wax OP was prepared and calendered on a 4 bowl "Z" calender at temperatures of 140°, 145°, 150°

and 155°C. The calendered sheet was press laminated at 175°C to a thickness of 0.250 inch. The resulting block was clear and of very pale yellow colour, whereas a control block prepared in the same way but which did not contain either component (b) or component (c) was yellow-brown in colour.

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EXAMPLES 12—16

Five polymer compositions were prepared, each containing 100 parts of Breon 112 and 50 parts of di-octyl phthalate, a well-known plasticiser. The following table shows the nature and the amounts of the components (a), (b) and (c) in each composition. Breon 112 is a homopolymer of vinyl chloride having a "K" value of approximately 70.

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Example	Component (a)	Component (b)	Component (c)
12	0.75 parts of each of calcium stearate, magnesium stearate and zinc stearate	0.2 parts of lauryl thioglycollate	0.2 parts of N-lauroyl p-amino phenol
13	"	"	0.2 parts of 2,2 ¹ methylene bis (4-methyl 6-tertiary butyl phenol)
14	1 part of barium stearate and 0.5 parts cadmium stearate	0.2 parts of nonyl thioglycollate	0.2 parts of N-stearoyl p-amino phenol
15	"	"	0.2 part of bisphenol A
16	2 parts dibutyl tin maleate prepolymer	0.2 parts of zinc diethyl dithiocarbamate	0.2 parts of N-lauroyl p-amino phenol

Each composition was milled at 150—155°C for 10 minutes.

Each of the milled sheets obtained in Examples 12 and 13 was pressed at 180°C for 20 minutes, and remained a pale yellow colour. A control composition which did not contain either component (b) or (c) was treated in an identical manner and after pressing was of a green colour with black decomposition spots visible.

Each of the milled sheets obtained in Examples 14 and 15 was pressed at 185°C for 30 minutes, and the specimens produced were of a pale yellow colour. A control specimen, produced in an identical manner from a composition which did not contain either component (b) or (c), was a bright yellow colour.

The milled sheet obtained in Example 16 was pressed at 185°C for 45 minutes, and the specimen produced was of a very pale yellow colour. A control specimen produced from a composition which did not contain either component (b) or (c) was yellow in colour.

WHAT WE CLAIM IS:—

1. A polymer composition which comprises a mixture of a major proportion of one chlorine-containing polymer sensitive to heat and/or light degradation, selected from chlorine-containing homopolymers and chlorine-containing copolymers, together with a system consisting of at least one member drawn from each of categories (a), (b) and (c), wherein (a) represents a stabiliser for chlorine-containing polymers which comprises an organic-metallic compound in which the metal atom is lithium, sodium, potassium, magnesium, calcium, zinc, strontium, cadmium, barium, aluminium, tin or lead, or a mixture of any

two or three such organic-metallic compounds, provided that the stabiliser does not solely comprise barium laurate or cadmium laurate or dibasic lead phthalate, nor contain a mixture comprising organic-barium, organic-cadmium and organic-tin compounds, (b) represents a sulphur-containing organic or organo-metallic compounds having a boiling point at atmospheric pressure not below 200°C, and that does not contain chains of more than two consecutive sulphur atoms and in which at least one of the sulphur atoms has at least one lone electron pair, excepting mercapto-benzimidazole, mercapto-benzothiazole and their salts, and (c) represents an organic antioxidant capable of inhibiting chain reactions leading to degradation in the chlorine-containing polymer or co-polymers, provided also that the members drawn from each category are chemically distinct, such that at least three separate chemical compounds are present in admixture with the chlorine-containing polymer or polymers.

2. A polymer composition as claimed in claim 1, wherein the monomer from which the chlorine-containing homopolymer is derived or at least one of the monomers from which the chlorine-containing copolymer is derived is a chlorine-containing olefinically unsaturated compound.

3. A polymer composition as claimed in claim 1 wherein the chlorine containing copolymer is derived from a chlorine-containing olefinically unsaturated monomer and vinyl acetate.

4. A polymer composition as claimed in claim 2 or 3 wherein the chlorine-containing olefinically unsaturated compound is vinyl

chloride, vinylidene chloride or cis- or trans-1:2-dichloroethylene.

5. A polymer composition as claimed in claim 1, wherein the chlorine-containing polymer is polyvinyl chloride prepared by an emulsion, suspension or bulk polymerisation method.

6. A polymer composition as claimed in claim 1, wherein the chlorine-containing polymer is a post-chlorinated polymer.

7. A polymer composition as claimed in claim 6, wherein the post-chlorinated polymer is polyvinyl chloride or a vinyl chloride copolymer which has been further chlorinated in suspension under the influence of ultra-violet irradiation, to give a product having a chlorine content in the range of 55 to 70%, by weight and containing only a minor proportion of 1:1-dichloroethylene units based on the total weight of dichloroethylene units present.

8. A polymer composition as claimed in claim 4, wherein the chlorine-containing polymer is a vinyl chloride and vinylidene chloride copolymer containing from 3 to 4 per cent by weight of vinylidene chloride units.

9. A polymer composition as claimed in claim 3 or 4, wherein the chlorine-containing polymer is a vinyl chloride and vinyl acetate copolymer containing about 10% by weight of vinyl acetate units.

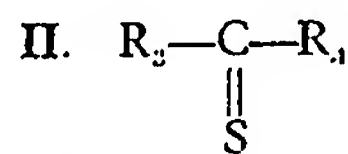
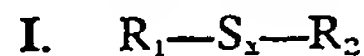
10. A polymer composition as claimed in claim 4, wherein the chlorine-containing polymer is a graft or block copolymer derived from two or more of the chlorine-containing olefinically unsaturated compounds specified in claim 4.

11. A polymer composition as claimed in claim 9, wherein the vinyl chloride and vinyl acetate copolymer has been prepared by an emulsion, suspension or solution method.

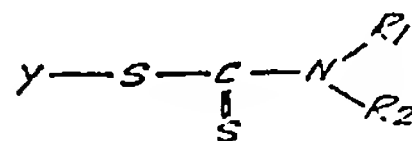
12. A polymer composition as claimed in any one of claims 1 to 11, wherein the component (a) is an organo-tin, organo-thio-tin, organo-barium or organo-cadmium compound, or a mixture of an organo-tin compound and an organo-thio-tin compound, or a mixture of an organo-barium compound and an organo-cadmium compound, or a mixture of an organo-calcium compound, an organo-magnesium compound and an organo-zinc compound.

13. A polymer composition as claimed in claim 12, wherein the component (a) is dibutyl tin maleate prepolymer, cadmium or barium stearate, dibutyl tin β -mercapto-propionate/2-ethyl-hexyl maleate, or dibutyl tin bis (2-ethyl-hexyl thioglycollate).

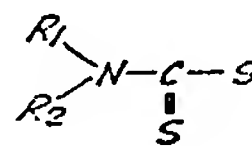
14. A polymer composition as claimed in any one of claims 1 to 12, wherein the component (b) is a compound of the formula I, II or III.



(iii)



wherein x represents 1 or 2, R_1 and R_2 are the same or different and each represents an alkyl, alkenyl, alkynyl, aralkyl, aryl, alkyl-aryl or cycloalkyl radical, or a radical containing a heterocyclic ring containing nitrogen, oxygen or sulphur, or R_1 or R_2 , but not both, may represent a hydrogen atom, R_3 and R_4 are the same or different and each represents a radical as defined for R_1 and R_2 , or each represents a primary or secondary alkyl-aralkyl-, aryl-, alkyl-aryl- or cycloalkyl-amino radical, or R_3 and R_4 , but not both, may represent a hydrogen atom, and Y represents the group



or a metal atom as defined in claim 1 with respect to component (a), the remaining groups attached to a metal atom having a valency greater than one being one or more of the groups R_1 , R_3 , R_4 and Y, but where Y is not a metal atom.

15. A polymer composition as claimed in claim 14, wherein the component (b) is an alkyl or aryl sulphide, a mercaptocarboxylic acid or an ester or polyester thereof, a monothio or dithio dicarboxylic acid or an ester or polyester or anhydride thereof, a thio glycol or an ester or polyester or ether thereof, a hydroxy alkyl or aryl sulphide or an ester or ether thereof, an aromatic thiol, a thiourea, a dithio-carbonate or a dithio-carbamate.

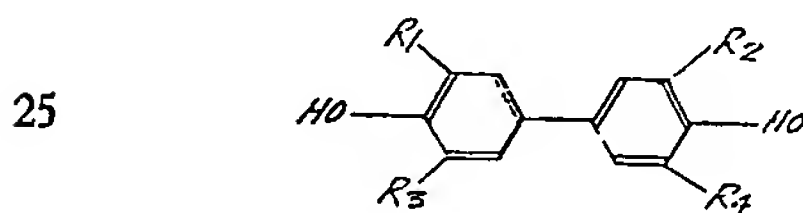
16. A polymer composition as claimed in claim 15, wherein the component (b) is thioglycollic acid, lauryl thioglycollate, nonyl thioglycollate, thiodiglycollic acid, dithiodiglycollic acid, β mercapto-propionic acid, $\beta\beta^1$ thiodipropionic acid, $\beta\beta^1$ dithiodipropionic acid, dilauryl $\beta\beta^1$ thiodipropionate, $\beta\beta^1$ dihydroxy-ethyl sulphide, bis (n-dodecyloxy-ethyl) sulphide, 4-4' thio bis(6-tertiary butyl meta-cresol), dibutyl tin bis (dibutyl dithiocarbamate), zinc bis (dibutyl dithiocarbamate), zinc diethyl dithiocarbamate, dibutyl tin dithiodiglycollate, naphthalene thiol, dibutyl tin bis (diphenyl dithiocarbamate), or dibutyl tin bis

(diphenyl thiourea dithiocarbamate) prepared from a dichloro stannic compound, carbon disulphide and diphenyl thiourea.

17. A polymer composition as claimed in any one of claims 1 to 16, wherein the component (c) is a nuclear substituted phenol, an aromatic primary or secondary amine, an N-substituted p-amino phenol, or a compound containing a nitrogen heterocyclic ring in which the nitrogen atom bears a replaceable hydrogen atom.

18. A polymer composition as claimed in claim 16, wherein the component (c) is 2:6 di-tertiary butyl 4-methyl phenol, 2:4 dimethyl 6-tertiary butyl phenol, 2:2¹ methylene bis [4-methyl (or 4-ethyl) 6-tertiary butyl phenol], resorcinol monobenzoate, p-octyl phenyl salicylate, a bisphenol, a di-hydroxy-biphenyl, pentaerythritol, α -phenol indole, diphenylamine, N-stearoyl p-amino phenol, N-lauroyl p-amino phenol, or 4,4' thio bis 6-tertiary butyl meta-cresol.

19. A polymer composition as claimed in claim 18, wherein the di-hydroxy-biphenyl has the formula



where R_1 , R_2 , R_3 and R_4 each represents tertiary butyl, ethyl, or methyl.

20. A polymer composition as claimed in claim 1, wherein the chlorine-containing polymer is as defined in any one of claims 5, 8, 9 and 11, component (a) is a compound selected from dibutyl tin maleate, dibutyl tin bis (2 ethyl hexyl thioglycollate) and dibutyl tin β -mercapto-propionate/2-ethyl-hexyl-maleate, component (b) is a compound selected from dilauryl $\beta\beta^1$ thiodipropionate, lauryl thioglycollate, nonyl thioglycollate, naphthalene thiol, and $\beta\beta^1$ dihydroxy ethyl sulphide, and component (c) is a compound selected from 2:6 di-tertiary butyl 4-methyl phenol, resorcinol monobenzoate, p-octyl phenyl salicylate, N-stearoyl p-amino phenol, and 2:2¹ methylene bis (4-methyl 6-tertiary butyl phenol).

21. A polymer composition as claimed in any one of claims 1 to 20, wherein the amount of component (b) is within the range of from 0.001 to 3 per cent by weight, based on the weight of the polymer or polymers.

22. A polymer composition as claimed in any one of claims 1 to 21, wherein the amount of component (c) is within the range of from 0.001 to 3 per cent by weight, based on the weight of the polymer or polymers.

23. A polymer composition as claimed in any one of claims 1 to 22, wherein the ratio of the amount of component (b) to the amount of component (c) is within the range of from 1:4 to 4:1, calculated on the weights of components (b) and (c).

24. A polymer composition as claimed in claim 23, wherein the weight of the component (b) is substantially equal to the weight of the component (c).

25. A polymer composition as claimed in any one of claims 1 to 24, which also contains a processing aid (as hereinbefore defined).

26. A polymer composition as claimed in claim 25, wherein the processing aid comprises an acrylic compound.

27. A polymer composition as claimed in any one of claims 1 to 26, which also contains a metal sequestering agent.

28. A polymer composition as claimed in claim 27, wherein the metal sequestering agent is triphenyl phosphite or epoxidised soya bean oil.

29. A polymer composition as claimed in any one of claims 1 to 28, which also contains a colouring or toning pigment or a filler.

30. A polymer composition as claimed in claim 1 and substantially as described herein with reference to any one of Examples 1—8.

31. A polymer composition as claimed in claim 1 and substantially as described herein with reference to any one of Examples 9—16.

32. Articles when prepared from a polymer composition as claimed in any one of claims 1 to 31.

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